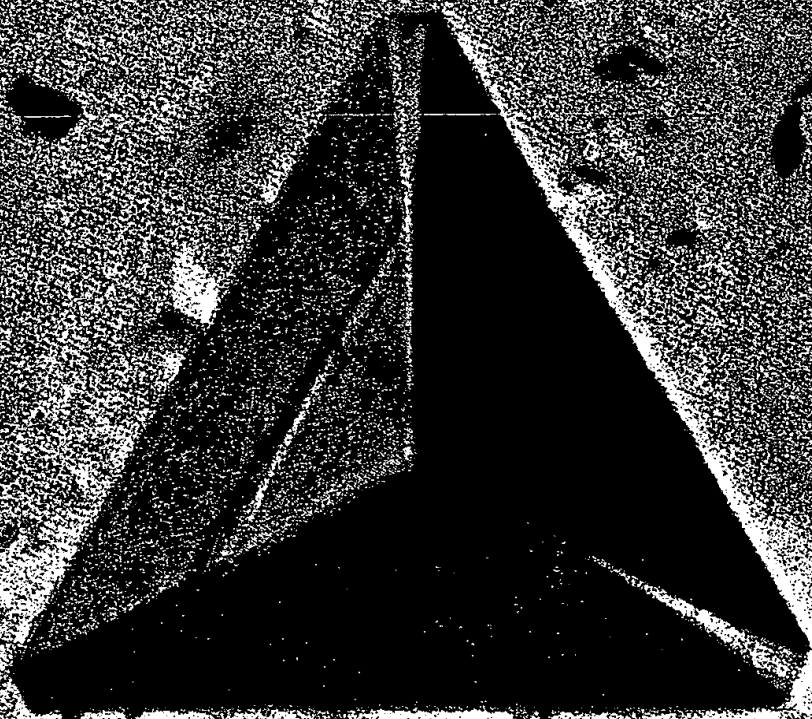


THEODORE L. BROWN
H. EUGENE LEMAY, JR.



Chemistry

The central science

2ND EDITION

Chemistry: The central science, 2nd edition
THEODORE L. BROWN ▲ H. EUGENE LEMAY, JR.

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TABLE 12.2 Equivalent-mass relationships

Reactant	Product	Reaction type	Mass of 1 mol of reactant (g)	Mass of 1 equivalent of reactant (g)
KMnO ₄	Mn ²⁺	Reduction (5 e ⁻)	158.0	158.0/5 = 31.6
KMnO ₄	MnO ₂	Reduction (3 e ⁻)	158.0	158.0/3 = 52.7
Na ₂ C ₂ O ₄	CO ₂	Oxidation (2 e ⁻)	134.0	134.0/2 = 67.0
H ₂ SO ₄	SO ₄ ²⁻	Acid (2 H ⁺)	98.0	98.0/2 = 49.0
Al(OH) ₃	Al ³⁺	Base (3 OH ⁻)	78.0	78.0/3 = 26.0

equivalent of reagent B. For example, in an oxidation-reduction reaction, 31.6 g of KMnO₄ is stoichiometrically equivalent to 67.0 g of Na₂C₂O₄ (refer to Table 12.2). Likewise, in an acid-base reaction, 49.0 g of H₂SO₄ is stoichiometrically equivalent to 26.0 g of Al(OH)₃.

Where KMnO₄ is reduced to Mn²⁺, thereby gaining five electrons, we have

$$1 \text{ mol KMnO}_4 = 5 \text{ equivalents of KMnO}_4$$

Therefore, if 1 mol of KMnO₄ is dissolved in sufficient water to form 1 L of solution, the concentration of the solution can be expressed as either 1 M or 5 N. Normality is always a whole-number multiple of molarity. In oxidation-reduction reactions, the whole number is the number of electrons gained or lost by one formula unit of the substance. In acid-base reactions the whole number is the number of H⁺ or OH⁻ available in a formula unit of the substance.

SAMPLE EXERCISE 12.5

What is the molarity and normality of a solution of H₂SO₄ made by dissolving 5.00 g of H₂SO₄ in enough water to make 200 mL of solution? The H₂SO₄ is used as an acid, forming SO₄²⁻.

Solution: The molecular weight of H₂SO₄ is 98.0 amu. The molarity is

Molarity =

$$\left(\frac{5.00 \text{ g H}_2\text{SO}_4}{200 \text{ mL soln}} \right) \left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.0 \text{ g H}_2\text{SO}_4} \right) \\ = 0.255 \frac{\text{mol H}_2\text{SO}_4}{\text{L soln}} = 0.255 M$$

Because H₂SO₄ has two available hydrogen ions, there are 2 chemical equivalents (equiv) in a mole and the normality is twice the molarity, 0.510 N:

$$\text{Normality} = \left(\frac{5.00 \text{ g H}_2\text{SO}_4}{200 \text{ mL soln}} \right) \left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) \\ \times \left(\frac{2 \text{ equiv H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.0 \text{ g H}_2\text{SO}_4} \right) \\ = 0.510 \frac{\text{equiv H}_2\text{SO}_4}{\text{L soln}} = 0.510 N$$

12.2 The solution process

A solution is formed when one substance disperses uniformly throughout another. With the exception of gas mixtures, all solutions involve substances in a condensed phase. We learned in Chapter 11 that substances in the liquid and solid state experience intermolecular attractive forces that hold the individual particles together. Intermolecular forces also operate between a solute particle and the solvent that surrounds it. Thus,

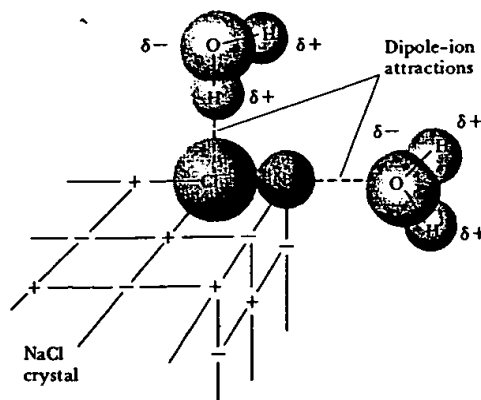


FIGURE 12.1 Interactions between H_2O molecules and the Na^+ and Cl^- ions of a NaCl crystal.

to understand solutions we must understand the kinds of attractive forces that exist between solute and solvent.

Any of the various kinds of intermolecular forces that we discussed in Chapter 11 can operate between solute and solvent particles in a solution. As a general rule, we expect solutions to form when the attractive forces between solute and solvent are comparable in magnitude with those that exist between the solute particles themselves or between solvent particles themselves. For example, the ionic substance NaCl dissolves readily in water. When NaCl is added to water, the water molecules orient themselves on the surface of the NaCl crystals as shown in Figure 12.1. The positive end of the water dipole is oriented toward the Cl^- ions, while the negative end of the water dipole is oriented toward the Na^+ ions. The ion-dipole attractions between Na^+ and Cl^- ions and water molecules are sufficiently strong to pull these ions from their positions in the crystal. Notice that the corner Na^+ ion is held in the crystal by only three adjacent Cl^- ions. In contrast, an Na^+ ion on the edge of the crystal has four nearby Cl^- ions, and a Na^+ ion in the interior of the crystal has six surrounding Cl^- ions. The corner Na^+ ion is therefore particularly vulnerable to removal from the crystal. Once this Na^+ ion

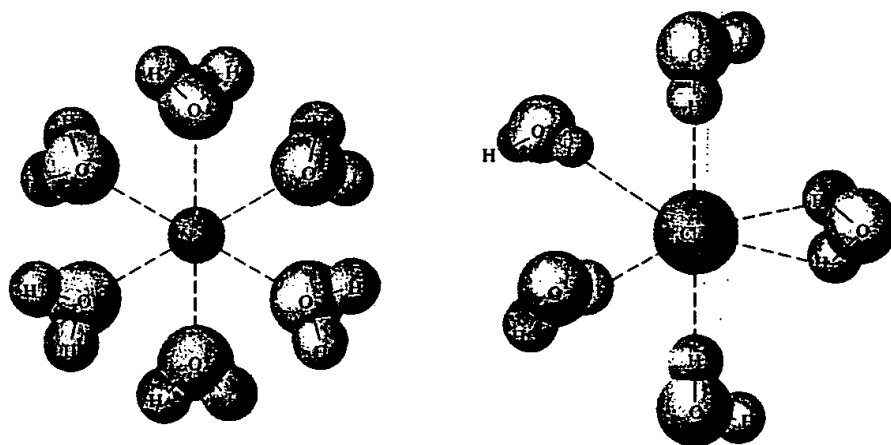
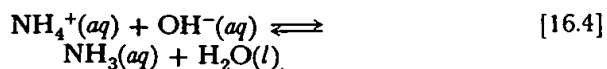


FIGURE 12.2 Hydrated Na^+ and Cl^- ions. The negative ends of the water dipole point toward the positive ion. The positive ends of the water dipole point toward the negative ion. We do not know whether one or both positive hydrogens touch the negative ion.



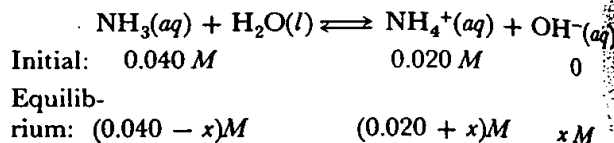
The Na^+ ion and Cl^- ion are not acidic or basic and are merely spectator ions. The reaction shown in Equation [16.4], involving a weak acid and a strong base, is virtually complete. Thus the 0.040 mol of OH^- consumes 0.040 mol of NH_4^+ producing 0.040 mol of NH_3 . The remaining NH_4^+ is the original amount minus the amount consumed: $0.060 \text{ mol} - 0.040 \text{ mol} = 0.020 \text{ mol}$. The total volume of the solution is the sum of the two original solutions: $0.60 \text{ L} + 0.40 \text{ L} = 1.00 \text{ L}$. Thus the concentrations of NH_3 and NH_4^+ are

$$[\text{NH}_3] = \frac{0.040 \text{ mol}}{1.00 \text{ L}} = 0.040 \text{ M}$$

$$[\text{NH}_4^+] = \frac{0.020 \text{ mol}}{1.00 \text{ L}} = 0.020 \text{ M}$$

The pH of a solution containing NH_4^+ and NH_3 can be calculated by considering the common-ion effect of NH_4^+ on the dissociation equilibrium of the weakly basic NH_3 . It can also be calculated by con-

sidering the effect of NH_3 on the dissociation equilibrium of the weakly acidic NH_4^+ . The same result will be obtained in either case. Using the reverse reaction of that shown in Equation [16.4], the pertinent species are summarized below with x defined as the equilibrium concentration of OH^- :



Substituting the equilibrium concentrations in the equilibrium-constant expression (K_b for NH_3 is taken from Appendix E) and assuming x to be small compared with 0.020 and 0.040 gives:

$$K_b = 1.8 \times 10^{-5} = \frac{(0.020)(x)}{0.040}$$

$$x = \frac{0.040}{0.020} (1.8 \times 10^{-5}) = 3.6 \times 10^{-5} = [\text{OH}^-]$$

$$\text{pOH} = -\log (3.6 \times 10^{-5}) = 4.44$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.44 = 9.56$$

16.2 Buffer solutions

Many aqueous solutions resist a change in pH upon addition of small amounts of acid or base. Such solutions are called **buffer solutions**, and are said to be buffered. Human blood, for example, is a complex aqueous medium with a pH buffered at about 7.4. Any significant variation of the pH from this value results in a severe pathological response and, eventually, death. As another example, the chemical behavior of seawater is determined in very important respects by its pH, buffered at about 8.1 to 8.3 near the surface. Addition of a small amount of an acid or base to either blood or seawater does not result in a large change in pH. Compare, for example, the behavior of a liter of seawater and a liter of pure water upon addition of 0.1 mL of 1 M HCl solution (1×10^{-4} mol of HCl), Figure 16.1. The pH of pure water changes by 3 units, from 7 to 4. The pH of seawater changes by only 0.6 pH units. Substances already dissolved in seawater limit the change in $[\text{H}^+]$ on addition of HCl.

Buffers ordinarily require two species, an acidic one to react with added OH^- and a basic one to react with added H^+ . It is, of course, necessary that these acidic and basic species not consume each other through a neutralization reaction. These requirements are fulfilled by an acid-base conjugate pair such as $\text{HC}_2\text{H}_3\text{O}_2$ - $\text{C}_2\text{H}_3\text{O}_2^-$ or NH_4^+ - NH_3 . The $\text{HC}_2\text{H}_3\text{O}_2$ - $\text{C}_2\text{H}_3\text{O}_2^-$ buffer mixture can be prepared by adding sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, to a solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. The NH_4^+ - NH_3 buffer mixture can be prepared by adding ammonium chloride, NH_4Cl , to a solution of ammonia, NH_3 . In general, a buffer mixture consists of an aqueous solution of an acid-base conjugate pair prepared by mixing a weak acid or base with a salt of that acid or base.

To understand how a buffer works, let's consider a solution of

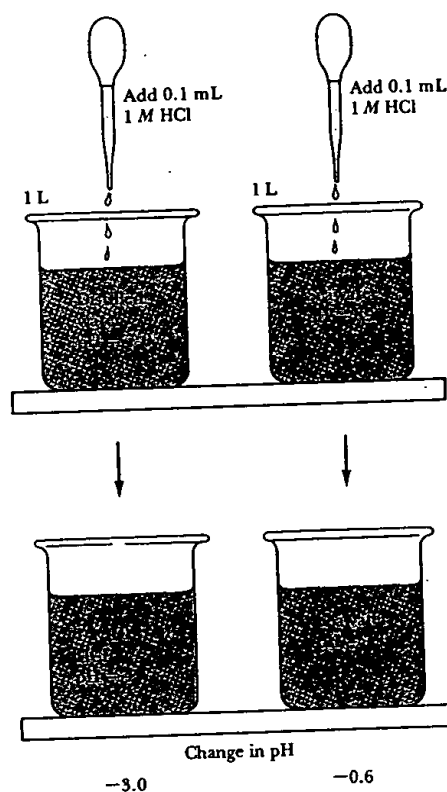
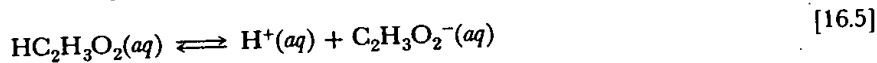


FIGURE 16.1 A comparison of the effect of added acid on the pH of distilled water as compared with the same quantity of seawater.

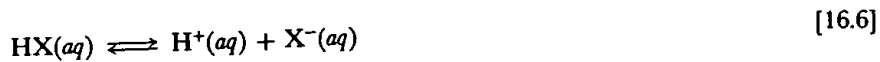
$\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. Ionization of $\text{HC}_2\text{H}_3\text{O}_2$ is governed by the following equilibrium reaction:



The $\text{C}_2\text{H}_3\text{O}_2^-$ in this equilibrium comes from both $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. This mixture can either react with surplus H^+ ions or release them, according to the circumstances. For example, if a small quantity of acid is added to the solution, the equilibrium shifts to the left; acetate ion reacts with the added H^+ . The solution thereby limits pH change due to added acid. On the other hand, if a small quantity of a base is added, it reacts with H^+ . This reaction causes the equilibrium of Equation [16.5] to shift to the right; $\text{HC}_2\text{H}_3\text{O}_2$ dissociates to form more H^+ . The solution thereby also resists change in pH due to added base.

Two important characteristics of a buffer are buffering capacity and pH. Buffering capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. This capacity depends on the amount of acid and base from which the buffer is made. The pH of the buffer depends on K_a for the acid and on the relative concentrations of the acid and base that comprise the buffer.

To better understand these characteristics, let's consider a buffer mixture consisting of a weak acid HX and a corresponding salt MX , where M could be Na^+ , K^+ , and so forth. The acid dissociation equilibrium is



and the corresponding acid dissociation constant expression is

$$K_a = \frac{[H^+][X^-]}{[HX]} \quad [16.7]$$

Let us now take the logarithm in base 10 of both sides of the equation:

$$\log K_a = \log [H^+] + \log \frac{[X^-]}{[HX]} \quad [16.8]$$

Multiplying through on both sides by -1 , we have

$$-\log K_a = -\log [H^+] - \log \frac{[X^-]}{[HX]} \quad [16.9]$$

Because $-\log K_a = pK_a$ and $-\log [H^+] = \text{pH}$, we have

$$pK_a = \text{pH} - \log \frac{[X^-]}{[HX]} \quad [16.10]$$

$$\text{pH} = pK_a + \log \frac{[X^-]}{[HX]} \quad [16.11]$$

In general,

$$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad [16.12]$$

This relationship, which is called the Henderson-Hasselbalch equation, is very useful in dealing with buffers. Notice that $\text{pH} = pK_a$ when the concentration of the acid and its conjugate base are equal. The pH range of most buffers is limited to the vicinity of the pK_a of the acid. For this reason, one usually tries to select a buffer whose acid has a pK_a close to the desired pH.

Although the pH of a particular buffer mixture depends on the relative concentrations of the acid and its conjugate base, its buffering capacity depends on the amounts of the acid and base. A 1-L solution that is 1 M in $\text{HC}_2\text{H}_3\text{O}_2$ and 1 M in $\text{NaC}_2\text{H}_3\text{O}_2$ will have the same pH as a 1-L solution that is 0.1 M in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.1 M in $\text{NaC}_2\text{H}_3\text{O}_2$. However, the first solution has a greater buffering capacity because it contains more $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$.

SAMPLE EXERCISE 16.4

What is the pH of a buffer mixture composed of equal concentrations of NH_4Cl and NH_3 ?

Solution: Using Equation [16.12], we have

$$\text{pH} = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

Because $[\text{NH}_3] = [\text{NH}_4^+]$,

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 1 \quad \text{and} \quad \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 0$$